1 INTRODUCTION

The physical and chemical properties of nanomaterials can differ significantly from those of the atomic-molecular or the bulk materials of the same composition. The uniqueness of the structural characteristics, energetics, response, dynamics, and chemistry of nanostructures constitutes the basis of nanoscience. Suitable control of the properties and response of nanostructures can lead to new devices and technologies. The themes underlying nanoscience and nanotechnology are twofold: one is the bottom-up approach, that is, the miniaturization of the components, as articulated by Feynman, who stated in the 1959 lecture that "there is plenty of room at the bottom" and the other is the approach of the self-assembly of molecular components, where each nanostructured component becomes part of a suprastructure.

The ability to assemble only the atoms and molecules needed to build the desired structure has been the domain of Nature and is referred to as the 'bottom-up' approach. Until we were able to 'see' the smaller detail, we did not know how Nature went about building structures. It has been the development of advanced 'measuring' instrumentation such as transmission electron- and scanning probe-microscopes that has allowed scientists and engineers to 'see' and 'manipulate' structure on the nanometer (nm) length scale. By controlling material structure at the nanoscale, properties can often be significantly enhanced. For example, we can exploit material properties that are much more surface-related rather than bulk controlled, including optical properties of metal oxides, gas transport properties of membranes, catalytic properties of nanoparticles; and the utilisation of these benefits have been some of the drivers for fabrication of structure on the nanoscale.

Nanoscience will be central to the next epoch of the information age. From the top ten advances in materials science at least five are directly related to nanoscience. Some people think that nanoscience is likely to revolutionize many areas of human activity, such as materials science, information processing, biotechnology, and medicine. In chemistry, nanotechnology tools such as scanning tunneling microscopy (STM) enable the study and manipulation of chemical reactions on the atomic scale, nanocatalytical processes can be initiated, and the bottom-up synthesis of organic as well as inorganic supramolecular structures for, e.g., molecular devices is revitalized. Nanoscience is a most interdisciplinary approach because all disciplines and areas converge at the nanoscale to the same basic principles and the same basic tools so that the frontiers between the disciplines even seem to disappear. It is well recognized that for the exploitation of nanoscience and nanotechnology one must understand the physics and chemistry of the nanoscale and one must learn how to make materials and functional devices.
Metal nano particles have attracted a great deal of attention in recent years due to their optical, physical and chemical properties that differentiates them from bulk material properties. Hence they find wide application in various fields like catalysis, photonics, optoelectronics, information storage, antibacterial applications, etc. Silver powders, having ultra fine and uniformly distributed particle size, are of considerable use in the electronics industry as thick film conductors in integrated circuits due to their unique properties such as high electrical and thermal conductivity, high resistance to oxidation. Apart from electronic applications, it has been known for centuries that silver has bactericidal properties. Silver is a safe and effective bactericidal metal because it is non-toxic to animal cells and highly toxic to bacteria such as *Escherchia coli* (*E. coli*) and *Staphylococcus aureas*.

With the emergence and increase of microbial organisms resistant to multiple antibiotics, and the continuing emphasis on health-care costs, many researchers have tried to develop new, effective antimicrobial reagents free of resistance and cost. Such problems and needs have led to the resurgence in the use of Ag-based antiseptics that may be linked to broad-spectrum activity and far lower propensity to induce microbial resistance than antibiotics. The antibacterial effects of Ag salts have been noticed since antiquity, and Ag is currently used to control bacterial growth in a variety of applications, including dental work and burn wounds.

Silver doped polymer fabrics, catheters and polyurethane are well known for their antibacterial functionality. Colloidal silver, nano silver coated fabric, nano silver metal oxide granules and nano silver coated ceramic materials are used for antibacterial applications. Nano silver in the form of powders as well as suspensions, due to the high surface to volume ratios, has been used in the above said applications as it enables the loading of small quantities of silver and thus makes the product cost effective.

The immobilisation of nanoparticles on matrix materials greatly increases the exposed surface area. The matrix material prevents aggregation of the nanoparticles and allows separation of the products from the catalyst particles. Typical matrix materials include: activated carbon, silica, and alumina; however, polymers are gaining increasing interest as matrix materials due to their ability to control particle growth as well as stabilize the resulting particles.

Polyelectrolytes, such as chitosan, are particularly interesting in metal nanoparticle synthesis due to their interactions with metal ions and metal nanoparticles. Chelation evenly disperses metal ions throughout the polymer. Subsequently, the dispersed metal ions can be reduced to a zerovalent state forming dispersed nanoparticles. The polymer then binds with the nanoparticles preventing catalyst leaching. These characteristics make polyelectrolytes ideal catalyst supports. The primary amines on chitosan are involved in metal ion chelation and nanoparticle immobilization.
Naturally occurring polymers such as lignin, chitosan and albumin are very effective protecting agents for nanoparticles of precious metals such as platinum, gold, and silver. Natural polymers with polar terminal groups like amine, hydroxyl, amide etc are a very useful class of protective agents. The effective stabilization of nanoparticles is achieved by immobilizing them into the natural polymer matrix by large number of polar terminal groups.

Lignin is a natural composite material in all vascular plants, providing the plant with strength and rigidity. It is a main component of vascular plants. Indeed, lignin is second only to polysaccharides in natural abundance, contributing 24 - 33\% and 19 - 28\%, respectively, to dry wood weights of normal softwoods and temperate-zone hardwoods. By decreasing water permeation across the cell wall, lignin renders the plant resistant to biodegradation as well as to environmental stresses. Lignin is an amorphous, aromatic, water insoluble, heterogeneous, three-dimensional, and cross-linked polymer with low viscosity. The molecular mass of lignin is high (600 - 1000 kDa), although not uniform, varying greatly within isolated samples.

The primary precursors for p-hydroxyphenyl, guaiacyl and syringyl units of lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, respectively. The monomers couple with the phenolic end groups of the growing lignin polymer, not with each other. Peroxidase and laccase catalyse the random polymerization. Lignin has no single repeating bond; phenylpropanoid units are linked together by more than ten different types of aryl ether and carbon-carbon linkages.

In 1823, Odier found a material with the same general properties as fungine in the cuticle of beetles and designated it "chitin" after the Greek word "chiton" that denotes "coat of mail" in reference to the cuticle. Chitin is a structural polysaccharide widely found in nature. Chitin occurs as highly ordered microfibrils in many species, in a variety of arrangements, from diatom spines to cell wall components of many fungi and yeast. It is also a principal component in the exoskeleton of insects and marine invertebrates such as Arthropoda and Mollusca. Chitin is a homopolymer of 1-4 linked 2-acetamido-2-deoxy-\(\beta\)-D-glucopyranose, although some of the glucopyranose residues are deacetylated and occur as 2-amino-2-deoxy-\(\beta\)-D-glucopyranose. When chitin is deacetylated to about 50\% of the free amine form, it is referred to as chitosan.

Chitin is considered the second most plentiful biomaterial, following cellulose. The annual production of chitin biomass has been estimated at \(1 \times 10^{13}\) kg worldwide. This has led to considerable scientific and technological interest in chitin and chitosan. Chitosan has become the preferred commercial form of this material as it is more tractable than chitin. Isolated chitins are highly ordered copolymers of 2-acetamido-2-deoxy-\(\beta\)-D-glucose and 2-amino-2-deoxy-\(\beta\)-D-glucose. The occurrence of the latter is explained by the fact that in vivo chitin is covalently linked.
to proteins via the nitrogen atom of approximately one repeating unit out of ten, therefore upon
isolation a degree of deacetylation close to 0.10 is found. Chitosan is also under study for medical
and pharmaceutical uses. It has also become a popular nutritional dietary additive.

Serum albumin is the most abundant and the most studied of the proteins of the circulation.
One of the first proteins to be recognized, its name derives from the early name for proteins,
albumen, derived from the Latin word *albus*, white-in this case, white of an egg. Albumin is one
of the longest known and probably the most studied of all proteins. Its manifold diverse functions
have attracted the interest of scientists and physicians for generations. Its applications are many,
both in clinical medicine and in basic research. Albumin is the most abundant soluble protein in
the body of all vertebrates and is the most prominent protein in plasma. Some of its physiological
properties have been recognized since the time of Hippocrates.

The physiological importance of albumin has been known for years. Albumin is synthesized
by the liver and represents close to 50% of hepatic protein production. It is the major oncotically
active plasma protein, contributing about 60-80% of the plasma colloid osmotic pressure (COP),
and, therefore, of major importance in the regulation of transvascular fluid fluxes. Since albumin
reversibly binds anions as well as cations, it is a major transport protein for metals, free fatty
acids, hormones, enzymes, drugs, etc. Furthermore, albumin has detoxifying effects, acts as a
scavenger of free radicals, and exerts inhibitory effects on platelet aggregation.

The present work deals with the development of a series of photoresponsive environment
-friendly systems based on biopolymeric core materials. The biopolymeric cores used in this study
are lignin, chitosan and bovine serum albumin. The core systems having free hydroxylgroups
were functionally modified with selected photochromic molecules such as 1-(5-(4-dimethylamino-
benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, 2-oxo-2H-1-benzopyran-3-carboxylic acid,
3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl) butyric acid.

2 OBJECTIVES

The purpose of the current research work is to explore the synthesis of photochemically modified
natural polymers with photoresponsive and light fastening properties. It also aimed to explore
the synthesis of silver nanoparticle dispersed natural macromolecular systems such as lignin,
chitosan and BSA and assess their utility for bio applications. In view of these challenges, the
main objectives of the present work are:

- To synthesise or to use photoactive chromophoric systems such as 1-(5-(4-dimethylamino-
benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, 2-oxo-2H-1-benzopyran-3-carboxylic
  acid, 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl) bu-
tyric acid

- To generate Chromophore - labelled natural polymers and to develop light harvesting antenna systems based on the natural polymers such as lignin, chitosan and bovine serum albumin
- To synthesise silver nanoparticles for photochemical and biological studies
- To develop nanoparticle - dispersed natural polymers modified with photoresponsive groups
- To characterise the chromophoric systems, biopolymers functionalised with chromophores, metal nanoparticles and nanoparticle - dispersed polymeric cores by FT IR, UV - Visible and $^1H$ NMR spectroscopic techniques, fluorescence measurements, electron microscopic analysis and by thermal analysis
- To study the light fastening ability of the polymer bound chromophoric systems
- To study the fluorescence emission behaviour of the functionally modified natural polymers
- To assess the thermal stability of the functionally modified and nanoparticle dispersed natural polymeric systems
- To conduct studies on the antibacterial and antifungal activities of the silver nanoparticle dispersed natural polymers against various bacterial and fungal strains
- To synthesise sodium doped lithium niobate nanostructures and stabilise these nanostructures in biopolymers

3 DESCRIPTION OF THE WORK

The biopolymeric core systems selected for the study are lignin, chitosan and bovine serum albumin, all are having free hydroxyl groups. Four different chromophoric systems were employed to develop the photochemically modified biopolymers. The modification was achieved by functional transformation such as esterification. All the chromophoric systems selected for the present study have free carboxyl functions. These carboxylic functional groups were attached to the biopolymeric cores through esterification of the free alcoholic functions of the cores by DCC coupling. The newly developed systems were soluble in polar solvents, ‘nature friendly’ and ‘Green’ in their properties. The esterified products were isolated, purified by column chromatography or membrane dialysis. The systems thus developed are: lignin - 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, lignin - 2-oxo-2H-1-benzopyran-3-carboxylic acid, lignin - 3-((E)-(4 - aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid, lignin - 4-(1-pyrenyl)butyric acid,
chitosan - 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, chitosan - 2-oxo-2H-1-benzopyran-3-carboxylic acid, chitosan - 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid, chitosan - 4-(1-pyrenyl)butyric acid, BSA - 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, BSA - 2-oxo-2H-1-benzopyran-3-carboxylic acid, BSA - 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and BSA - 4-(1-pyrenyl)butyric acid. All the products were characterised by FT IR, UV - Visible and $^1$H NMR spectroscopic techniques, fluorescence measurements and by thermal analysis. Spectral studies show that all these photochromic systems have successfully introduced into the cores and thermal studies indicate optimum stability for all the products.

The light fastening properties of the chromophoric systems and the biopolymeric cores functionalised with the chromophores were studied by continuous irradiation under visible radiant energy. The results were analysed and compared. The light fastening analysis of 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid and its biopolymer bound esters show that the light fastening of 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid was greatly enhanced when attached to biopolymers. For the monomeric system, 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid, a strong absorption in the visible region was observed at 465 nm and there was a decrease in the intensity up on irradiation with sun light. For the lignin bound chromophoric system, there was no appreciable change in the intensity of absorption on several hours of irradiation and the $\lambda_{max}$ in the visible region shows a red shift. The light fastening properties of the chromophoric system was enhanced when attached to chitosan and bovine serum albumin also. There was a slight decrease in the $\epsilon_{max}$ of the functionalised chitosan and bovine serum albumin on prolonged irradiation under sunlight, but decrease in intensity is lower than that of the low molecular weight chromophoric system. The emission behaviour of the monomeric dye, 1-[5-(4-dimethyl amino-benzylidine-4-oxo-2-thioxo-thiozolidine-3-yl]) acetic acid and lignin, chitosan and bovine serum albumin functionalised with the chromophoric system were studied. It is evident from the the emission behaviour of different systems that the fluorescence efficiency was enhanced by attaching the chromophore onto biopolymer backbone. The emission maximum was red shifted on binding to lignin and chitosan core and a blue shift on attaching to BSA.

Light fastening properties of 2-oxo-2H-1-benzopyran-3-carboxylic acid (coumarin-3-carboxylic acid) and its biopolymer bound analogues were studied. There was a decrease in the absorption maximum of the coumarin carboxylic acid on exposure to visible radiant power indicating $[2\pi + 2\pi]$ cycloaddition and thereby shortening of the conjugated $\pi$-system. But the photodimerisation was greatly prevented when the chromophoric system attached to the biopolymers such as lignin.
and chitosan. The functionalisation of 2-oxo-2H-1-benzopyran-3-carboxylic acid with lignin and chitosan augment the photochemical stability of the chromophore by keeping the chromophoric systems far apart from each other. But the light fastening behaviour of BSA analogue was in a similar fashion as that of monomeric chromophore. The free movement of the protein backbone support the $[2\pi + 2\pi]$ cycloaddition. The photophysical properties of the photoluminescent biopolymers were compared to the monomeric chromophore 2-oxo-2H-1-benzopyran-3-carboxylic acid. All the systems were irradiated at the same excitation wavelength at room temperature. The fluorescence emission properties are entirely different when lignin, chitosan and albumin are functionalised with the same chromophore 2-oxo-2H-1-benzopyran-3-carboxylic acid. The emission maximum was red shifted to 14 nm and 10 nm, when the chromophore attached to lignin and chitosan respectively.

The the azo chromophore 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and its biopolymer bound analogues were irradiated under visible radiant energy for 6 hrs. The results were analysed and compared. There was a notable red shift of the absorption peak in the visible region, when the azo chromophore 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid was anchored with the biopolymers. The $\pi \rightarrow \pi^*$ band is much stronger in polymer bound analogues than that in a simple azo molecule. As the result of binding of the chromophoric system to polymers the band due to the $\pi \rightarrow \pi^*$ transition shifted to a shorter wavelength; however, the band due to the $n \rightarrow \pi^*$ transition appeared at longer wavelength. Also the trans-to-cis photoisomerization efficiency was getting lower as the chromophore bind to the polymer system, perhaps due to hindrance of condensed structures. The absorption band corresponding to $\pi \rightarrow \pi^*$ transition was shifted to a shorter wavelength, 318 nm and the band due to the $n \rightarrow \pi^*$ transition appeared at longer wavelength, 485 nm when attached to lignin. In the case of chitosan functionalised with 3-[(E)-(4-aminophenyl) diazenyl] naphthalen-2-ol carboxylic acid, the absorption band corresponding to $\pi \rightarrow \pi^*$ transition was shifted to a shorter wavelength, 309 nm and the band due to the $n \rightarrow \pi^*$ transition appeared at longer wavelength, 484 nm. But in the case of bovine serum albumin functionalised with 3-[(E)-(4-aminophenyl) diazenyl] naphthalen-2-ol carboxylic acid, the absorption band corresponding to $\pi \rightarrow \pi^*$ transition was shifted to a shorter wavelength of 311 nm and the band due to the $n \rightarrow \pi^*$ transition appeared at longer wavelength of 484 nm. The fluorescence emission spectra of lignin, chitosan and BSA functionalized with 3-[(E)-(4-aminophenyl) diazenyl] naphthalen-2-ol carboxylic acid and the monomeric dye were recorded and compared. The fluorescence emission properties were enhanced when the chromophore was functionalized with lignin, chitosan and bovine serum albumin.

Pyrene is the fruit fly of photochemists. Its unique properties have inspired researchers from
many scientific areas, making pyrene the chromophore of choice in fundamental and applied photochemical research. The light fastening properties of the chromophore 4-(1-pyrenyl)butyric acid and its biopolymer esters were studied by irradiating these systems under visible radiant energy for a long time. The photochemical stability of the chromophoric system, 4-(1-pyrenyl)butyric acid, was appreciably increased when it was attached to lignin, chitosan and albumin. The $\epsilon_{\text{max}}$ exhibited by the chromophore showed a gradual decrease on prolonged irradiation. Lignin, chitosan and BSA functionalised with 4-(1-pyrenyl)butyric acid are photochemically stable systems and there was no appreciable change in the intensity of absorption on several hours of irradiation under visible light. Excitation (324 nm) of ground-state monomers (M) gives rise to excited-state monomers (M$^*$) with typical emission maxima at 375 and 395 nm. When M$^*$ interacts with a spatially proximal M in a precise configuration, the resulting M$^*$-M dimer results in excimer emission (M$^{**}$) at 419 nm. Compared to monomer fluorescence, excimer emission is red-shifted and lacks the fine structure which arises from vibrational transitions.

The phase transition behaviors of the precursor polymers, precursor chromophores and the functionalized polymers were studied by using the differential scanning calorimetry (DSC). The thermal stability of the polymers was characterized by the thermogravimetric analysis (TGA). To observe the thermal behavior of biopolymers, chromophores and biomolecules functionalised with chromophores, Differential Scanning Calorimetry (DSC) measurements, using a heating rate of 10 $^\circ$C min$^{-1}$, were performed. Different endothermic and exothermic transitions were studied and compared. TG - DTA studies were performed on biopolymers, chromophores and biopolymers functionalised with chromophoric systems and the results were compared. The DSC and TG - DTA studies of lignin, chitosan and bovine serum albumin functionalised with chromophores showed that the thermal behaviour of the chromophoric systems were enhanced when these system were anchored by biopolymers. Esters of the chromophoric systems with chitosan showed the maximum thermal stability than the esters with lignin and bovine serum albumin.

One of the main objective of our work was to synthesise silver nanoparticle and sodium doped lithium niobate nanostructures and to stabilise these nanostructure by encapping in biopolymers. In our work, silver nanoparticles were synthesised by the reduction of silver acetate by dodecyl amine. It is a single step reduction reaction of silver acetate in which dodecylamine acts as the reducing agent and the capping agent. Sodium doped lithium niobate nanostructures were synthesised by sol-gel method. These nanoparticles were stabilised through the encapsulation of these particles into biopolymers and functionalised biopolymers. There are limited applications for colloidal formulation of metal nanoparticles. So we encapsulated these colloidal nanoparticles into biopolymer matrices. The hydroxyl and amino functional groups of the biopolymers were
used to stabilise these nanostructures. All the products were characterised by FT IR, UV-Visible, 
$^1$H NMR and scanning electron microscopic analysis and thermal studies. These studies show
that these nanostructures were well encapsulated into these biopolymers. In these systems ab-
sorption peaks near to 400 nm is due to the characteristic surface plasmon resonance (SPR)
band of silver nanoparticles. The surface plasmon resonance of silver nanoaprticles depends on
the size and shape of the particles. The scanning electron microscopic studies showed that the
nanostructures were well encapsulated and stabilised by biopolymer matrices. Biopolymers im-
part biocompatibility to these nanostructures. The coupling of biomolecular entities and materials
at the nanoscale has the potential to revolutionize many fields of science and technology, poten-
tially having a significant impact on current biomedical technologies, nanoelectronics, and related
areas. Because nanoparticles and biomolecules typically have the same nanometer length scale,
they are natural companions in hybrid systems. These materials are extremely attractive candi-
dates for use in biotechnological and microbiological systems.

In the present work, we encapsulated silver nanoparticles into biopolymers functionalised
with 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl)butyric
acid. The intensity of absorption of chromophoric systems in the UV-Visible spectra were no-
tably enhanced and the $\lambda_{max}$ were red shifted. The intensity of the luminescence emission
of silver nanoparticle encapsulated biopolymers functionalised with 3-((E)-(4-aminophenyl) di-
azenyl) naphthalen-2-ol carboxylic acid was deceased by the quenching of fluorescence emission
of chromophoric systems by metal nanoparticles. But the photophysical properties of biopoly-
mers functionalised with 4-(1-pyrenyl)butyric acid were greatly enhanced when silver nanopar-
ticles were encapsulated into it. To observe the thermal behavior of silver naoparticle encap-
sulated biomolecules functionalised with 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol car-
boxylic acid and 4-(1-pyrenyl)butyric acid, Differential Scanning Calorimetry (DSC) measure-
ments, using a heating rate of 10 °C min$^{-1}$, were performed. A notable enhancement in the
thermal properties was showed by silver nanoparticles encapsulated lignin functionalised with
3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl)butyric acid.

The antibacterial activity of silver nanoparticles encapsulated biopolymers were investigated
on Staphylococcus aureus, Serratia marcescens, Pseudomonas aeruginosa, Escherichia coli and
Klebsiella pneumoniae. The silver nanoparticles encapsulated biopolymers were tested for their
antibacterial activity by the agar diffusion method. These bacteria were seeded in agar plates
by the pour plate technique and to this plates discs of previously loaded by silver nanoparticle
encapsulated biopolymers were introduced and incubated. The formation of a clear zone (re-
stricted bacterial growth) around the discs is an indication of antibacterial activity. The activity of
silver nanoparticle encapsulated lignin and bovine serum albumin against gram-positive bacteria *Staphylococcus aureus* was 27 mm and 26 mm respectively. The antibacterial activity studies of silver nanoparticle encapsulated lignin and bovine serum albumin against gram-negative species like *Serratia marcescens*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Klebsiella pneumoniae* showed an average zone of inhibition of 25.6 and 24.5 mm for silver nanoparticle encapsulated lignin and bovine serum albumin respectively. This study showed that silver nanoparticles encapsulated biopolymers exhibit efficient antibacterial activity and these systems can be used for antibacterial applications.

The fungicidal property of silver nanoparticle encapsulated lignin and bovine serum albumin was tested against different fungal strains. The fungal strains used in this study are *Aspergillus flavus*, *Aspergillus niger*, *Pencillium janthinellum*, *Pencillium purpurogenum*, *Chrysosporium sps* and *Mucor circinelloides*. The well method was used to test the anti fungal activity. The growth pattern were observed, the diameter of the clear zone was measured of those it showed. The data was tabulated, and photographic records were taken. Silver nanoparticle encapsulated lignin showed maximum activity against *Pencillium janthinellum* with an average inhibition zone of 40.0 mm and it was least active against *Pencillium purpurogenum* with an average inhibition zone of 27.2 mm. But in the case of silver nanoparticle encapsulated bovine serum albumin, the maximum activity showed against *Mucor circinelloides* with an average inhibition zone of 29.2 mm and they are least active against *Chrysosporium sps* with an average inhibition zone of 23.0 mm. This study showed that silver nanoparticles encapsulated biopolymers exhibits efficient fungicidal activity and these systems can be used as fungicides.

### 4 OUTLINE OF THE DISSERTATION

The thesis is organized into seven chapters. The first chapter is the introductory chapter of the dissertation. This chapter gives an idea of the core materials, chromophoric systems, nanoparticle dispersed polymeric cores with a special reference to their generation and applications. The important objectives are given in this chapter. A detailed literature review on naturally occurring polymers such as lignin, chitosan and albumin and nanoparticles with special reference to silver nanoparticles, its chemistry, material science and biological properties are sketched out in Chapter 2. The chapter describes the biosynthesis, properties and applications of these natural polymers and photochemistry of the chromophoric systems. It also gives a detailed description on nanoparticles, especially silver nanoparticle, including synthesis, characterization and applications. A detailed lists of references of the back literature is given at the end of the chapter.

Chapter 3 is the detailed description of the experimental methods. A general description of
the materials and various experimental protocols are included here. It describes the synthetic methods, purification and characterization techniques of individual products used in this work.

Chapter 4 presents the experimental results obtained on functionally modified lignin, chitosan and bovine serum albumin with four different chromophoric systems. Structural characterizations of the compounds are done by various spectroscopic techniques such as UV-visible, FT IR and $^1$H NMR spectroscopic methods. A detailed discussion on the spectral results of the four chromophoric systems, the three core systems and the twelve different coupled products are also given in this chapter. The results are discussed in detail and all the relevant references are cited.

Chapter 5 presents the studies on the photoresponsive properties such as light absorption and fluorescence emission of the functionally modified polymers. The light fastening ability of the photochemically modified polymeric systems was one of the main objectives. In this chapter we also discussed the results of thermal studies of the functionally modified polymeric core systems. A detailed discussion on the photochemistry, photophysics and thermal stability of the newly developed systems was included in this chapter.

Chapter 6 describes our studies on the synthesis of silver nanoparticles by reduction technique and characterization of their shape and size by SEM, TEM and UV visible spectroscopic analysis. The structural characterization and investigation of the photophysical properties of chromophore functionalized and nanoparticle dispersed natural polymers are included in this chapter. Antibacterial and antifungal property of the nanoparticle dispersed natural polymers is the focal point. The thermal stability of the nanoparticle dispersed natural polymers was also investigated. Sodium doped lithium niobate nanostructures (LNN) were synthesised and encapsulated into biomolecules. These results are also discussed in this chapter.

In Chapter 7 conclusions are drawn, and possible future extension to this work is discussed. Detailed lists of references are given at the end of each chapter.

5 CONCLUSION

Metal nanoparticles have attracted a great deal of attention in recent years due to their optical, physical and chemical properties that differentiates them from bulk material properties. Hence they find wide application in various fields like catalysis, photonics, optoelectronics, information storage, antibacterial applications, etc. Silver nanoparticles, having fine and uniformly distributed particle size, are of considerable use in the electronics industry as thick film conductors in integrated circuits due to their unique properties such as high electrical and thermal conductivity, high resistance to oxidation.

Lignin, arguably the second most abundant biomacromolecule existing in the plant kingdom,
is relatively inexpensive and widely available. Commercially, lignin is obtained as a byproduct of “wood-free” paper making. Primarily burnt as an energy source and as part of a complex chemical recovery system, some industrial processes consistently produce standard well-defined lignins. Chitin is a homopolymer of 1-4 linked 2-acetamido-2-deoxy-β-D-glucopyranose, although some of the glucopyranose residues are deacetylated and occur as 2-amino-2-deoxy-β-D-glucopyranose. When chitin is deacetylated to about 50% of the free amine form, it is referred to as chitosan. Chitin predominantly comes from crab and shrimp shells, but is also found in a myriad of other sources making it the most abundant natural polymer after cellulose. Albumin is the most abundant soluble protein in the circulatory system and contributes 80% to colloid osmotic blood pressure. These biopolymers have hydroxyl and amino functionalities and these functionalities are susceptible to functionalisation.

In this work functionalisation of biopolymers with different chromophores such as, 1-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo - thiazolidin - 3 - yl)-acetic acid - a chromophore with push-pull electron modulation, 2-oxo-2H-1-benzopyran-3-carboxylic acid, an azo chromophore 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl)butyric acid were done to develop a series of photoresponsive biopolymers. These functionalisation reactions were carried out through the DCC coupling of hydroxyl functionalities of biopolymers with carboxylic acid group of chromophoric systems. These products were purified with column chromatography and characterised with UV-Visible, FT IR and $^1$H NMR spectroscopic methods.

The light absorption, light fastening and fluorescence properties of all the chromophoric and biomolecules functionalised with chromophores were studied. Absorption maximum of the chromophore was red shifted in each case and the intensity of the absorption was greatly enhanced when attached to biopolymers. A maximum red shift was observed when the chromophoric system was attached to lignin. Aromatic groups present in lignin impart more photochemical resistance to the chromophoric system. There was an enhancement in the intensity of absorption of all the chromophoric systems when bound to lignin, chitosan and bovine serum albumin.

In this work, the thermal properties of biopolymers and chromophoric systems were studied in detail. The thermal stability of chromophoric systems increased when attached to biopolymers. The chitosan bound analogue was the most thermally stable system.

Silver nanoparticle and sodium doped lithium niobate nanostructures were synthesised and stabilised these nanostructures by encapsulating these colloidal nanoparticles into biopolymer matrix. Biopolymers impart biocompatibility to the system. Metal nanoparticles can be so unstable that if their surfaces touch, they will fuse together, losing their special shape and properties. The development of Polymer Stabilized Metal Nanoparticles is one of the most promising solutions
to the metal nanoparticles stability problem. The incorporation of metal nanoparticles into the biopolymer matrix offers enhanced performance for both the host and the guest. These materials are extremely attractive candidates for use in biotechnological and microbiological systems. The products were characterised by FT IR, $^1$H NMR, UV-Vis, SEM, TG-DTA and DSC analysis.

A new class of metal nanoparticle impregnated and functionally modified natural polymers were prepared using the encapsulation approach. Lignin, chitosan and bovine serum albumin functionalised with 3-[(E)-(4-aminophenyl) diazenyl] naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl)butyric acid were encapsulated with silver nanoparticles. The products were characterised by FT IR, $^1$H NMR, UV-Vis, SEM, TG-DTA and DSC analysis. Photochemical, photo-physical and thermal properties of all the systems were studied.

The work can be extended to explore the biological and biomedical utility of the systems developed in this work. This need more in vitro and in vivo investigations.

6 REFERENCES


